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Perturbation-Theoretic Approach to Potential-Energy Curves of Diatomic Molecules*

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A perturbation theory is developed whereby the diatomic molecular potential energy $W(R)$ as a function of the internuclear distance R is expressed, for R near R_e, as a power series in the parameter $\lambda=1-(R_e/R)$,

$$W(\lambda)=w_0+\sum_{n=1}^{\infty}(w_n-w_{n-1})\lambda^n.$$

Truncations of this series have the form of finite power series in R^{-1}. The quantities w_n are obtained simply as perturbation energies for a purely kinetic-energy perturbation at R_e, by setting up the problem in confocal elliptic coordinates, in which the kinetic-energy part of the Hamiltonian is R^{-2} times an R-independent operator and the potential-energy part is R^{-1} times an R-independent operator. Expressions for the successive vibrational force constants k_e, l_e, m_e, $\cdots$, are given, and it is shown how it happens, through cancellation of effects in the molecule near R_e against effects in the separated atoms, that truncation of the power series in λ at the λ^2 level is often a good approximation, as has been shown empirically.

I. INTRODUCTION

The Fues potential,[1]

$$W(R)=W_0+(W_1/R)+(W_2/R^2), \tag{1}$$

is known to be a reasonably good representation of potential-energy curves for diatomic molecules for R near R_e, in spite of the fact that at first glance the R^{-1}, R^{-2} dependence of the potential seems overly strong for covalently bonded systems.[2-4] The force constants predicted by this potential are

$$k_e=(d^2W/dR^2)_e=-W_1/R_e^3=2W_2/R_e^4, \tag{2}$$

$$l_e=(d^3W/dR^3)_e=-(6/R_e)k_e, \tag{3}$$

$$m_e=(d^4W/dR^4)_e=(36/R_e^2)k_e, \tag{4}$$

and so on, which give the result

$$(k_em_e/l_e^2)^{1/2}=1. \tag{5}$$

These predictions are surprisingly accurate. For example, for a large number of species the quantity in Eq. (5) averages about 0.86.[2,3,5] Trends in observed l_e, m_e, etc., values in going from one molecule to another, or from one state to another state in a particular molecule, are almost always reproduced by Eqs. (3) and (4). It is even true that predictions from these formulas are quantitatively about as good as calculations with Hartree–Fock wavefunctions, or as predictions from many alternative well-known potential functions.[6] Also, extension of Eq. (1) to include the R^{-3} term gives results so significantly better than Eq. (1) itself that an excellent representation of the potential energy near R_e by a series of the form,

$$W(R)=\sum_{n=0}^{N}\frac{W_n}{R^n}, \tag{6}$$

seems likely, very generally.[7]

An additional, quite compelling argument in favor of Eq. (1), or its extension, Eq. (6), as a form for the potential function, is that a physical interpretation of the most important parameters, W_1 and W_2, is not difficult to give. From the molecular virial theorem and Eq. (6) it follows that the electronic potential energy has the form, in the region of validity of Eq. (6),

$$V(R)=2W_0+\frac{W_1}{R}-\frac{W_3}{R^3}+\cdots+(2-N)\frac{W_N}{R^N}, \tag{7}$$

while the electronic kinetic energy $T(R)$ has the form

$$T(R)=-W_0+\frac{W_2}{R^2}+\frac{2W_3}{R^3}+\cdots+(N-1)\frac{W_N}{R^N}. \tag{8}$$

The leading terms in $V(R)$ are the constant "core" term $2W_0$ plus a Coulomb-like term W_1/R, with a classical form for the latter. The leading terms in $T(R)$ are the constant "core" term $-W_0$ plus a "valence" term W_2/R^2, the latter having the R dependence that

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[1] E. Fues, Ann. Physik **80**, 367 (1926). See also L. D. Landau and E. M. Lifshitz, *Quantum Mechanics, Non-relativistic Theory* (Pergamon Press, Ltd., London, 1959), p. 128.

[2] R. G. Parr and R. F. Borkman, J. Chem. Phys. **46**, 3683 (1967).

[3] R. F. Borkman and R. G. Parr, J. Chem. Phys. **48**, 1116 (1968).

[4] R. G. Parr and R. F. Borkman, J. Chem. Phys. **49**, 1055 (1968), preceding paper.

[5] A. A. Frost and B. Musulin, J. Am. Chem. Soc. **76**, 2045 (1954).

[6] See Tables II and III of Ref. 3.

[7] See Table IV of Ref. 3.

would be predicted from naive application of the uncertainty principle.[3] Simple point-charge models can be constructed which reproduce the empirical values of W_1 and W_2 and mimic the essential physical features of $T(R)$ and $V(R)$ as described.[4]

These results and these considerations suggest that a formal theory which is able directly to incorporate inverse powers of R near R_e may be of value. In the present paper we derive and discuss a formal perturbation approach whose truncations are equivalent to Eq. (6). By employing confocal elliptic coordinates and treating a molecule with internuclear separation R as a perturbation of the molecule at R_e with perturbation parameter $1-(R_e/R)$, we obtain a perturbation scheme involving only a kinetic-energy perturbation. We show that truncation of the series to give the potential of Eq. (1) is an exact consequence of a natural assumption about the cancellation of certain terms in going from the separated atoms to the molecule.

II. PERTURBATION EXPANSION

The Born–Oppenheimer electronic Hamiltonian operator for a diatomic molecule may be written in the form

$$\mathcal{H}=R^{-2}\hat{t}+R^{-1}\hat{v}, \tag{9}$$

where R is the internuclear distance, and $\hat{t}$ and $\hat{v}$ are the kinetic-energy and potential-energy operators expressed in confocal elliptic coordinates, for unit R.[8] For the present discussion we do not need the detailed formulas for $\hat{t}$ and $\hat{v}$. It is important only that they may be treated as independent of R, and that implicit variations with R of the coordinates theemselves need not be considered.[9] The potential term includes the nuclear–nuclear repulsion. The eigenvalue $W(R)$ of the equation,

$$\mathcal{H}\Psi=W\Psi, \tag{10}$$

is then the conventional potential-energy function for the molecule as a function of R. We are of course interested in many different eigenfunctions and eigenvalues of this equation. The following argument applies to any diatomic molecule in any state having a minimum in its potential energy $W(R)$ at a distance R_e so long as no degeneracies occur at that distance.

At the equilibrium R_e, the Hamiltonian will be

$$\mathcal{H}_e=(R_e)^{-2}\hat{t}+(R_e)^{-1}\hat{v}, \tag{11}$$

with eigenfunctions Ψ_{ek} and eigenvalues W_{ek}. We suppose that we have solved this problem exactly and we undertake to solve Eq. (10) by Rayleigh–Schrödinger perturbation theory with $\mathcal{H}_e$ as the zero-order Hamiltonian.

If we introduce the parameter

$$\lambda=1-(R_e/R), \tag{12}$$

we may rewrite Eq. (9) as

$$\mathcal{H}=\mathcal{H}(\lambda)=[(1-\lambda)^2/R_e^2]\hat{t}+[(1-\lambda)/R_e]\hat{v}. \tag{13}$$

If we now divide Eq. (10) by $(1-\lambda)$, which is permissible if $\lambda\neq 1$, we would have the Schrödinger equation to be solved,

$$[(1-\lambda)(\hat{t}/R_e^2)+(\hat{v}/R_e)]\Psi=[W/(1-\lambda)]\Psi. \tag{14}$$

For $\lambda=0$ the equation is

$$[(R_e)^{-2}\hat{t}+(R_e)^{-1}\hat{v}]\Psi_{ek}=W_{ek}\Psi_{ek}, \tag{15}$$

presumed already solved. Our problem thus is equivalent to the problem of a purely kinetic-energy perturbation, a change in Planck's constant, or a change in electronic mass.

We take λ as a perturbation parameter and, for λ small enough, expand Ψ and $W/(1-\lambda)$ as a power series in λ,

$$\Psi=\Psi_e+\lambda\Psi^{(1)}+\cdots, \tag{16}$$

$$W/(1-\lambda)=w_0+w_1\lambda+w_2\lambda^2+w_3\lambda^3+\cdots. \tag{17}$$

Then we find, suppressing subscripts k where appropriate,

$$w_0=W_e, \tag{18}$$

$$w_1=-\bar{T}_e=W_e, \tag{19}$$

$$w_2=-\langle\Psi_e\,|\,\hat{t}/R_e^2\,|\,\Psi^{(1)}\rangle$$
$$=\sum_{n\neq k}[|\langle\Psi_{ek}\,|\,\hat{t}/R_e^2\,|\,\Psi_{en}\rangle|^2/(W_{ek}-W_{en})], \tag{20}$$

$$w_3=-\langle\Psi^{(1)}\,|\,(\hat{t}/R_e^2)-\bar{T}_e\,|\,\Psi^{(1)}\rangle$$
$$=-\sum_{m\neq k}\sum_{n\neq k}\frac{\langle\Psi_{ek}\,|\,\hat{t}/R_e^2\,|\,\Psi_{em}\rangle\langle\Psi_{em}\,|\,(\hat{t}/R_e^2)-\bar{T}_{ek}\,|\,\Psi_{en}\rangle\langle\Psi_{en}\,|\,\hat{t}/R_e^2\,|\,\Psi_{ek}\rangle}{(W_{ek}-W_{em})(W_{ek}-W_{en})}, \tag{21}$$

where it has been assumed that $\langle\Psi_e\,|\,\Psi^{(1)}\rangle=0$, and where all energies W_{em}, W_{en} are those appropriate for the equilibrium internuclear distance R_e for state k.

Performing the multiplication of $(1-\lambda)$ needed to give W itself from Eq. (17), we obtain

$$W=w_0+\sum_{n=1}^{\infty}(w_n-w_{n-1})\lambda^n, \tag{22}$$

with the first few w_k given by Eqs. (18)–(21). This completes the formal solution of the problem. For the

[8] For example, see P. Phillipson, J. Chem. Phys. **39**, 3010 (1963); C. A. Coulson and A. C. Hurley, *ibid.* **37**, 448 (1962).

[9] T. L. Cottrell and S. Paterson, Trans. Faraday Soc. **47**, 233 (1951).

force constants of Eqs. (2)–(4), we obtain

$$\tfrac{1}{2}R_e^2k=w_2-w_1, \tag{23}$$

$$\tfrac{1}{6}R_e^3l_e+R_e^2k_e=w_3-w_2, \tag{24}$$

$$(1/24)R_e^4m_e+R_e^3l_e+\tfrac{3}{2}R_e^2k_e=w_4-w_3, \tag{25}$$

and so on. Truncation of the series of Eq. (22) at some power of λ and rearrangement as a series in $1/R$ will give a potential-energy curve of the form of Eq. (1) or Eq. (6).

Equation (23) was given by Clinton in 1963.[10] Clinton's formulation of the problem led him to a study of an R-dependent quantity $S_k(R)$.[10] He observed that *for an atom* ($R=0$ or $R=\infty$) this quantity was exactly equal to the total energy. By Eq. (20) we have $S_k(R_e)=w_2$, and we may generalize Clinton's result if we imagine applying all of the above formulas to the motion of an atom from the distance R_e to the distance R from another point, with that point and the center of the atom being taken as the foci for an elliptic coordinate system, as above. Then since the energy does not change, all force constants are zero, and Eqs. (18), (19), and (23)–(25) give

$$w_n(\text{atom})=w_1(\text{atom})$$
$$=W_e(\text{atom}) \qquad \text{for all } n. \tag{26}$$

Another way of proving this is to consider the effect of a kinetic perturbation, $-\lambda T$, on an atom. This may be considered as a change in electronic mass from m to $\mu=m/(1-\lambda)$. The electronic energy then changes from $W(m)$ to $W(\mu)=(\mu/m)W(m)=1/(1-\lambda)W(m) = W(m)+\lambda W(m)+\lambda^2W(m)+\cdots$. There is a corresponding result for molecules, $W(\mu, R)=(\mu/m)W(m, \mu R/m)$, but this is of no particular utility.

III. TRUNCATIONS

The condition under which the series of Eq. (22) will truncate exactly to a quadratic in R^{-1} is clear: It is necessary and sufficient that

$$w_n=w_{n-1}=0, \qquad n\geq 3. \tag{27}$$

If we assume this, we obtain

$$W=W_e+(w_2-W_e)\lambda^2. \tag{28}$$

This is just the potential of Eq. (1), with the identifications

$$W_0=w_2, \tag{29}$$

$$W_1=-2R_e(w_2-W_e), \tag{30}$$

$$W_2=R_e^2(w_2-W_e). \tag{31}$$

[10] W. L. Clinton, J. Chem. Phys. **38**, 2339 (1963). Clinton defines the quantity $S_k(R)$ as

$$S_k(R)=\sum_{n\neq k}\frac{|\langle\Psi_k|\hat{t}/R^2|\Psi_n\rangle|^2}{W_k-W_n}.$$

TABLE I. Energy coefficients in the λ expansion method.[a]

Molecule	State	w_2-w_1[b]	w_3-w_2[b,c]
AlH	Ground	0.50	−0.15
B_2	Ground	1.04	−0.70
BaH	Ground	0.46	−0.05
BO	Ground	2.27	−1.44
C_2	Ground	1.88	−1.37
CH	Ground	0.64	−0.14
CO	Ground	2.78	−1.93
CuH	Ground	0.54	−0.15
H_2	Ground	0.93	+0.15
H_2^+	Ground	0.24	+0.10
HCl	Ground	0.93	−0.20
K_2	Ground	0.17	−0.01
Li_2	Ground	0.21	+0.02
LiH	Ground	0.30	+0.03
N_2	Ground	3.15	−2.59
NO	Ground	2.42	−2.29
Na_2	Ground	0.19	+0.02
O_2	Ground	1.97	−1.95
C_2	$A\,^3\Pi_g$	2.08	−1.16
CH	$A\,^2\Delta$	0.65	−0.30
CH	$B\,^2\Sigma^-$	0.57	−0.14
CH	$C\,^2\Sigma^+$	0.62	−0.40
N_2	$a\,^1\Pi_g$	2.02	−1.96
N_2	$B\,^3\Pi_g$	2.09	−1.96

[a] See text, Eqs. (17) and (22), for definitions of the tabulated quantities, all of which are given in atomic units.

[b] Determined from experimental data using Eqs. (23) and (24) of the text. Data on k_e, l_e, R_e are taken from G. Herzberg, *Spectra of Diatomic Molecules* (D. Van Nostrand Co., Inc., New York, 1950), 2nd ed.

[c] For the conventional perturbation expansion in powers of $\mu=(R/R_e)-1$ (Ref. 12), the coefficients of the μ^3 term for a few representative molecules in their ground state are as follows: H_2^+: −0.38, Li_2: −0.40, O_2: −5.88, Na_2: −0.35, NO: −7.13, HCl: −2.25. The coefficient of μ^2 is the same as the coefficient of λ^2.

To the extent that the assumption of Eq. (27) is valid, the theoretical structure of the Fues potential is revealed by these formulas.

Of course the relations of Eq. (27) can be valid only approximately at best. But they are in fact obeyed reasonably well. What counts for the force constants, we can see from Eqs. (22)–(25), is whether the quantities w_n-w_{n-1} are small *relative to* the quantity w_2-w_1. For $n=3$ this is often so, as is shown in Table I for a number of species. Even when the quantities w_n-w_{n-1} are not small relative to w_2-w_1, Eq. (22) may converge quite well for R near R_e because of the smallness of λ.

The approximate cancellations of Eq. (27) would follow from the hypothesis that as far *as these quantities are concerned*, the molecule is much like a pair of independent atoms, since for atoms Eq. (27) follows exactly from the previous Eq. (26). One need not assume that the atoms are in states appropriate for $R=\infty$; they may be in promoted valence states appropriate for R near R_e. We leave unexplored for the

TABLE II. Electronic energy of the ground state of H_2^+ as given by the quadratic approximation.[a]

R	$-W(R)_{exact}$[b]	$-W(R) = -W_e - \frac{1}{2}R_e^2 k_e \lambda^2$	| Error |
1.0	0.4518	0.3974	0.0544
1.2	0.5290	0.5114	0.0176
1.4	0.5700	0.5649	0.0051
1.6	0.5909	0.5898	0.0011
1.8	0.6003	0.6001	0.0002
2.0	0.6026	0.6026	0
2.2	0.6008	0.6009	0.0001
2.4	0.5965	0.5969	0.0004
2.6	0.5908	0.5917	0.0009
2.8	0.5843	0.5859	0.0016
3.0	0.5776	0.5798	0.0022
4.0	0.5461	0.5513	0.0052
5.0	0.5244	0.5287	0.0043
6.0	0.5120	0.5114	0.0006

[a] All quantities in atomic units.

[b] Data taken from D. R. Bates, K. Ledsham, and A. L. Stewart, Phil. Trans. Roy. Soc. (London) **A246**, 215 (1953).

present the precise connections between atomic and molecular w_n.

IV. DISCUSSION

The foregoing argument appears to establish the theoretical basis for the potential of Eq. (1), as a potential of wide and general applicability for diatomic molecular species near R_e. It would seem, for instance, that the formulas of Eqs. (2)–(5) are likely to hold, to reasonable accuracy, whenever a diatomic molecular state is bound, whatever the detailed valence-theoretic description of the binding is.[11]

Alternative perturbation expansions about equilibrium are of course possible. The expansion in powers of the parameter $\mu=(R/R_e)-1$ has been well investigated,[12] but it lacks the simplicity of the expansion in powers of $\lambda=1-(R_e/R)$ we have here put forward. Relations among higher-order potential constants and lower-order potential constants do not appear in the expansions in μ. The possibility of attaching physical meaning to successive coefficients W_n in the expansion of Eq. (6), already exemplified by construction of a simple model of the quadratic form,[4] lends confidence to the reasonableness of the λ expansion. Table II shows the effectiveness of the quadratic form for the energy for H_2^+, Eq. (28), over a large R range with w_2 determined from R_e and k_e.

Extensions of the argument, both in the context of perturbation theory and in the context of simple models, to the truncated cubic form including a term W_3/R^3, may be worthwhile. There is an extraordinary result in the literature: For H_2^+ a potential of the form of Eq. (6), including the cubic term, gives an energy within 10^{-5} a.u. of the true energy for 15 points on the exact potential near R_e.[13] The results already reported for other molecules also encourage one to expect high accuracy at the cubic level.[7]

Actual calculations by the perturbation method here proposed, or its variational analogues, would not be easy, but it is notable that kinetic-energy matrix elements between wavefunctions at a single internuclear separation are all that enter the perturbation calculations. It would be interesting to try some calculations by simplified forms of the method using limited-basis-set atomic orbitals and the molecular-orbital method. Even more interesting, perhaps, will be to try to extract from the perturbation-theoretic formulas for the potential constants, Eqs. (29)–(31), the quantum-theoretical structure of the empirical charge and bond-order entities introduced in the simple models described in the accompanying paper.[4]

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[11] For example, these results should hold for such species as He–He at long range. See the review of experimental results given by R. B. Bernstein and J. T. Muckerman, University of Wisconsin, Theoretical Chemistry Institute Rept. WIS-TCI-200, January 1967.

[12] W. Byers Brown, Proc. Cambridge Phil. Soc. **54**, 251 (1958). See also L. Salem, J. Chem. Phys. **38**, 1227 (1963).

[13] I. Sandeman, Proc. Roy. Soc. (Edinburgh) **55**, 72 (1935).